Synthesis and X-ray crystal structure of 3-cyclopentadienyl- 9-(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane

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It is a great pleasure and a privilege for the authors to be able to dedicate this paper to Professor Mikhail Grigor'evich Voronkov, Member of the Russian Academy of Sciences, on the occasion of his 80th birthday in recognition of his outstanding contributions to organoelement chemistry.

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Abstract

Electrophilic mercuration of 3-η^5-cyclopentadienyl-1,2-dicarba-3-cobalta-*closo*-dodecaborane **1** with $(AcO)_2Hg$ in CH_2Cl_2/AcOH (7:1) leads mainly to 9-acetomercuro-cobaltacarborane **2**. In addition, 8-mono- and 9,12-dimercurated products **3** and **4** were isolated in small yields. The X-Ray structural analysis of **2** reveals the Hg–B bond length of 2.10(1) Å.

Keywords: Cobaltacarborane, 3-cyclopentadienyl-9-(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane, mercuration, synthesis, X-ray, ^{11}B NMR

Introduction

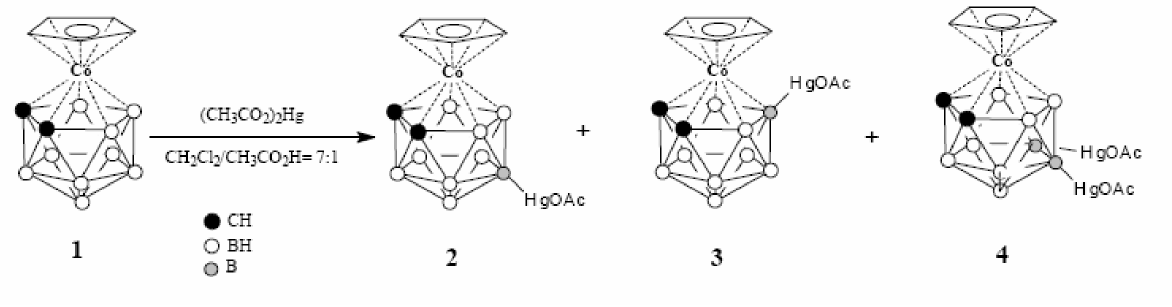
Previously, we have found that direct electrophilic mercuration of icosahedral carboranes $C_2B_{10}H_{12}$ takes place only with a strong electrophilic reagent such as $(CF_3CO_2)_2Hg$ in CF_3CO_2H affording B-mercuricarborane salts. Substitution occurs mainly at position 9 of the icosahedron, i.e. at the position most remote from the *o*-carborane carbon atoms.[1-4]

On the other hand, electrophilic reagents react with icosahedral metallacarboranes giving rise to substitution at position 8 in the open face of the dicarbollyl ligand or to the mixture of 8-, 9- and 12-substituted metallacarboranes.[5,6] However, Zakharkin et al.[7] have shown that mercuration of 3-η^5-cyclopentadienyl-1,2-dicarba-3-ferra-*closo*-dodecaborane leads exclusively to the substitution in position 9 of metallacarborane cage.

Results and Discussion

The purpose of this work is the synthesis of a monomercurated cobaltacarborane by electrophilic mercuration, its isolation, and the structure proof by X-ray analysis.

Mercuration of 3-η^5-cyclopentadienyl-1,2-dicarba-3-cobalta-*closo*-dodecaborane **1** takes place under milder conditions than mercuration of o-carborane. The reaction of **1** with $(AcO)_2Hg$ in a 7:1 $CH_2Cl_2/AcOH$ mixture led to its mercuration and yields 9- and 8-monosubstituted compounds **2** and **3** and 9,12-dimercurated product **4**.



Scheme 1

In order to avoid a formation of polymercurated and large amounts of dimercurated product, an excess (20%) of **1** was used. Compounds **2**, **3** and **4** were separated by column chromatography on silica gel (yields 60, 14 and 9% respectively). The structure of 3-η^5-cyclopentadienyl-9-(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane **2** was confirmed by X-ray diffraction study, ^{1}H and ^{11}B NMR spectra. A composition of **3** and **4** and the positions of substitution in them were determined by ^{11}B NMR spectra and elemental analysis.

X-ray diffraction study of **2** (Figure 1) shows that the geometry of the metallacarborane framework in this molecule is similar to that in 3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane.[8] In our previous work9 we reported the structure of 8-chlormercuro-3,6-bis(η5-cyclopentadienyl)-3,6-dicobalta-1,2-dicarba-*closo*-dodecaborane with the Hg-B bond length of 2.106 Å which appears to be very similar to the Hg(1)-B(9) bond length in **2** (2.10(1) Å). Our search through the Cambridge Structural Database[10] yielded only two structures with the Hg-B σ-bonds involving polyhedral borane clusters, namely the cationic complex bis(μ2-hydroxo)-(1,7-dicarbaboradodecaborane-9,10-diyl)dimercury (2.101 and 2.096 Å)[11] and the macrocyclic complex cyclo-tris(bis-(t-butyldimethylsilyl)-*m*-dicarbaundecaborane(8)-mercury (2.187 and 2.120 Å).[12] It is noteworthy, however, that the Hg-B distances in the last complex may be lengthened due to steric overcrowding in the macrocycle. The Hg(1)-O(1) bond distance of 2.149(9) Å is slightly longer than the typical values observed in the structures of trifluoroacetatomercury(II) derivatives, e.g. 2.121 Å in trifluoroacetatophenylmercury13 or 2.099 Å in trifluoroacetato-2,4,6-trineopentylphenylmercury.[14]

The geometry of the Co atom coordination environment is remarkably similar to that in the above mentioned classical metallacarborane species $CpCo(1,2\text{-}C_2B_9H_{11})$:$_8$ the Co-C$_{carb}$ distances are just barely shorter than Co-B, the C_2B_5 "open face" is planar within 0.006 Å, and the two 5-

membered rings are in a staggered conformation, the torsion angle B(7)X(1)X(2)C(14) involving the centroids of the C_2B_3 and the Cp rings (X(1) and X(2)) being equal to –40.2°. The C_2B_3/Cp dihedral angle is equal to 4.2°.

The crystal packing of **2** features a short intermolecular Hg···Hg contact (3.491(2)Å) between the Hg atoms of two molecules related by the two-fold axis. However, the distances of this range are rather common for Hg(II) derivatives and may hardly indicate anything but the normal Van der Waals contact between the metal atoms, which are low-coordinate, and therefore, much more easily exposed to intermolecular contacts than most of the other usually high-coordinated metals.

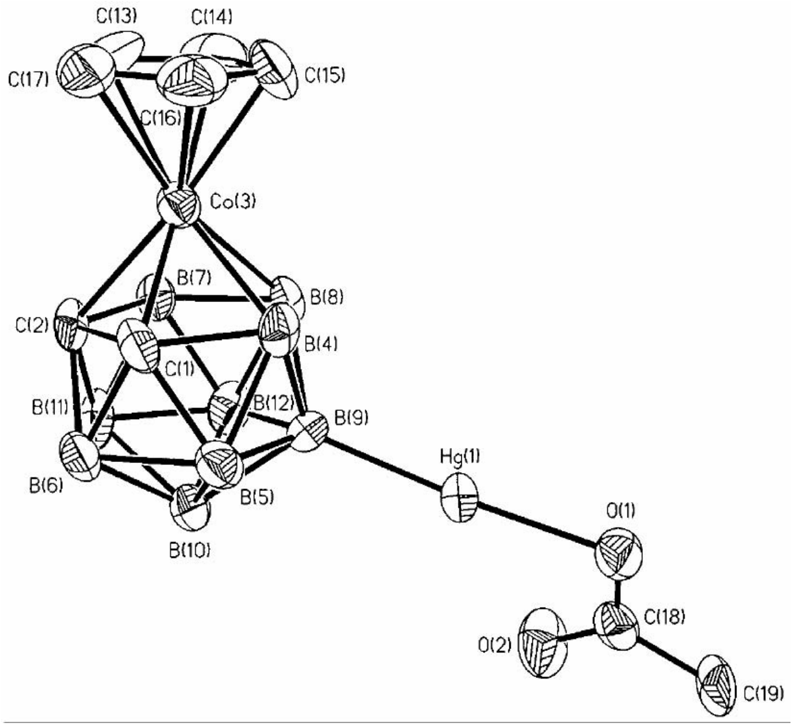


Figure 1. Molecular structure of 3-cyclopentadienyl-9-(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane (**2**). Selected bond distances (Å) and angles (deg.): Hg(1)-B(9) 2.10(1), Hg(1)-O(1) 2.149(9), O(1)-C(18) 1.31(2), O(2)-C(18) 1.21(2), Co(3)-C(1) 2.03(1), Co(3)-C(2) 2.03(1), Co(3)-B(4) 2.06(1), Co(3)-B(7) 2.05(1), Co(3)-B(8) 2.10(1), Co(3)-C_{Cp} 2.02÷2.07; B(9)-Hg(1)-O(1) 172.8(4), Hg(1)-O(1)-C(18) 105.4(8).

Experimental Section

General Procedures. The starting compound **1** was prepared by the previously reported procedure.[15] ^{1}H NMR and ^{11}B NMR spectra were recorded on a Bruker WP 200 SY spectrometer (200 MHz for ^{1}H and 64.2 MHz for ^{11}B) using TMS and $BF_3{\cdot}OEt_2$ as the external standards.

Mercuration of 3-η^5-cyclopentadienyl-1,2-dicarba-3-cobalta-*closo*-dodecaborane (1). Compound **1** (1.3 g, 5.66 mmol) was added to a solution of $(AcO)_2Hg$ (1.3 g, 4.70 mmol) in CH_2Cl_2/AcOH (7:1; 80 mL). The reaction mixture was stirred at 40 °C for 12 h and was then cooled. The solvent was evaporated in vacuo; the solid precipitate was dried over P_2O_5, dissolved in CH_2Cl_2, and purified by column chromatography on silica gel using CH_2Cl_2/hexane (2:1) as eluent gradually increasing CH_2Cl_2 up to 100%. Four yellow fractions were collected containing the starting material **1** (0.34 g), products **2**, **3**, and **4**.

3-Cyclopentadienyl-9-(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane (2). Yellow crystals (1.20 g, 60%), mp 165 °C. ^{1}H NMR (acetone-d_6): δ 5.98 (5H, s, H_{Cp}), 4.67 (1H, s, CH_{carb}), 4.52 (1H, s, CH_{carb}), 2.06 (3H, s, CH_3CO). ^{11}B NMR (acetone-d_6): δ 5.67 (1B, d, J_{BH} = 176 Hz), 2.30 (1B, d, J_{BH} = 163 Hz), –3.67 (1B, d, B(9),$^\#$ J_{BHg} = 2569 Hz), -5.30 (3B, m), –16.12 (2B, m), –22.93 (1B, d, J_{BH} = 176 Hz). Anal. Calcd for $C_9H_{18}B_9CoHgO_2$ (515.04): C, 21.0; H, 3.5; B, 18.9; Hg, 38.9; Co, 11.4. Found: C, 20.7; H, 3.6; B, 18.7; Hg, 39.1; Co, 10.9.

X-ray analysis of 2. $C_9H_{18}B_9O_2CoHg$, M = 515.04, monoclinic, space group *C2/c*, at 293 K a = 14.144(8), b = 13.889(9), c = 16.888(9) Å, β = 107.71(4)o, V = 3160(3) Å^3, Z = 8, d_{calc}. = 2.165 g/cm^3. The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer (T=293 K, graphite-monochromated MoKα radiation, λ = 0.71073 Å, θ/2θ scan technique, 2θ<56^o). The total of 3188 reflections was collected. The absorption correction (μ(MoKα) = 107.45 cm^{-1}) was applied with using the psi-scan technique ($T_{min/max}$ = 0.232/0.997). The structure was solved by direct methods and refined by the SHELXTL PLUS 5 program.[16] The H atoms of the carborane cage were located in the difference Fourier synthesis and included in the refinement in the isotropic approximation; the rest H atoms were placed in the geometrically calculated positions and refined in the riding model approximation. Final discrepancy factors were: R_1 = 0.0675 (on F for 2540 observed reflections with $I>2\sigma(I)$), wR_2 = 0.1941 (on F_2 for all 2986 independent reflections used in the refinement of 239 parameters). – Crystallographic data, final positional and thermal parameters for atoms and full list of bond lengths and angles for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-178487. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

3-Cyclopentadienyl-8-(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane (3). Yellow crystals (0.27 g, 14%), mp 197–198 °C. ^{11}B NMR (acetone-d_6): δ 6.64 (1B, d, B(8),$^\#$ J_{BHg} = 2728 Hz), 2.98 (1B, d, J_{BH} = 153 Hz), –5.41 (4B, m), –16.45 (2B, m), –21.2 (1B, d, J_{BH} = 152 Hz). Anal. Calcd for $C_9H_{18}B_9CoHgO_2$ (515.04): C, 21.0; H, 3.5; B, 18.9; Hg, 38.9; Co, 11.4. Found: C, 21.2; H, 3.4; B, 19.1; Hg, 38.6; Co, 11.6.

3-Cyclopentadienyl-9,12-bis(acetomercuro)-3-cobalta-1,2-dicarba-*closo*-dodecaborane (4). Yellow crystals (0.18 g, 9%), mp. 209–211 °C. ^{11}B NMR (acetone-d_6): δ 5.56 (1B, d, J_{BH} = 147 Hz), 2.12 (1B, d, J_{BH} = 150 Hz), –2.92 (2B, d, B(9,12), $^\#$ J_{BHg} = 2412 Hz), –5.39 (2B, m), –16.21 (2B, m), –24.45 (1B, d, J_{BH} = 202 Hz). Anal. Calcd for $C_{11}H_{20}B_9CoHg_2O_4$ (773.64): C, 17.1; H, 2.7; B, 12.5; Hg, 52.0. Found: C, 17.8; H, 3.1; B, 12.2; Hg, 53.4.

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References and Notes

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Position of substitution in the cobaltacarborane cage (for numeration see Fig. 1).

1. Bregadze, V. I.; Kampel, V. Ts.; Godovikov, N. N. *J. Organometal. Chem.* **1977**, *136*, 281.
2. Bregadze, V. I. *Proc. Indian Natl. Sci. Acad., Part A* **1989**, *55*, 414.
3. Bregadze, V. I.; Kampel, V.Ts.; Usyatinsky, A.Ya.; Godovikov N. N. *Pure & Appl. Chem.* **1991**, *63*, 835.
4. Bregadze V. I. *Chem. Rev.* **1992**, *92*, 209.
5. Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Polling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, Jr. L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.
6. Mátel, L.; Macášek, F.; Rajec, P.; Heřmánek, S; Plešek, J. *Polyhedron* **1982**, *6*, 511.
7. Zakharkin, L. I.; Kobak, V. V.; Antonovich, V.A. *Zh. Obshch. Khim.* **1983**, *53*, 2153 [*J. Gen. Chem. USSR (Engl. Transl.)* **1983**, *53*].
8. Smith, D. E.; Welch, A. J. *Organometallics* **1986**, *5*, 760.
9. Usyatinsky, A. Ya.; Khitrova, O. M.; Petrovskii, P. V.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T.; Bregadze, V. I. *Mendeleev Commun.* **1994**, 169.
10. Cambridge Structure Database. April 2000 Release.
11. Zheng, Z.; Knobler, C. B.; Curtis, C. E.; Hawthorne M. F. *Inorg. Chem.* **1995**, *34*, 432.
12. Zheng, Z.; Diaz, M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1995**, *117*, 12338.
13. Kamenar, B.; Penavic, M.; Hergold-Brundic, A. *Croat. Chem. Acta* **1984**, *57*, 145.
14. Lau, W.; Kochi, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 6720.
15. Plesek, J.; Stibr, B.; Hermanek, S. *Synth. Inorg. Met-Org. Chem.* **1973**, *3*, 291.
16. Robinson, W.; Sheldrick, G. M. In *Crystallographic computing 4 – techniques and new technologies*, Eds.: Isaacs, N. W.; Taylor, M. R. Oxford University Press: Oxford, 1988, p. 366.